

THE DETERMINATION OF A COMPLEX KINETIC EXPRESSION OF OIL SHALE PYROLYSIS USING COMBINED NON-ISOTHERMAL AND ISOTHERMAL TG

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The kinetic expression commonly used in the thermal analysis of oil shale pyrolysis was derived on the basis of a simple first order kinetic equation of kerogen decomposition. The activation energy, as well as the reaction rate constant of oil shale pyrolysis could be determined by using non-isothermal (NI) or isothermal (I) TG. However, the kinetic parameters determined by using either NI or I did not enable the good prediction of the kerogen conversion at other conditions.

The comparative results of the NI and I-TG of different oil shales are discussed in the study, as well as the effects of the so-called combined non-isothermal and isothermal TG (NI/I). The obtained results indicate that a mechanism must be postulated based on a complex reaction scheme which involves more than one simple reaction.

Keywords: kinetics, oil shale pyrolysis, TG

Introduction

A kinetic model of oil shale pyrolysis can be derived at different complexity levels, very often based on different thermal methods applied for detecting the effects of the thermal degradation of organic substances present in oil shale. The representation of the complex mechanism of the pyrolysis of oil shale by a single first-order reaction was commonly used, which has some advantages because only two parameters (the activation energy and frequency factor) and the stoichiometric equation of the simple reaction:



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in some cases determine the behaviour of oil shale pyrolysis very well. In Eq. (1), K denotes the kerogen present in the oil shale, P , the volatile products of pyrolysis (gas and oil), R , the residue or carbonaceous material, while f_1 and f_2 are the stoichiometric coefficients ($f_1+f_2=1$). Some data were recently published concerning the methodology for the determination of a multistep model based on the DSC and TG results of oil shale pyrolysis (Skala *et al.*, 1987, 1988, 1989, 1990).

In the present paper the comparative results of the NI- and I-TG of different oil shale samples are studied together with the results of combined NI/I-TG with the aim of a more detailed description of the pyrolysis process using only TG.

Experimental

Materials and methods

The investigations were performed with Aleksinac (A) and Knjazevac (K) (Serbia) and Creveney (CR, Toarcian basin, France) oil shale. They represent samples with different kerogen types; A is a kerogen with more paraffinic structure corresponding to type I, while the others are type II (CR) and type III (K) kerogens.

The experiments were done with a Perkin Elmer TGS-2 instrument using approximately 10 mg of powdered sample (<61 μm) prepared by grinding and sieving.

Non-isothermal pyrolysis

Non-isothermal pyrolysis was performed over the range 303–873 K in nitrogen (flow rate 25 cm^3/min) and at heating rates of 5, 10 and 20 K/min.

Isothermal analysis

The results of recently published isothermal TG (Skala *et al.*, 1988) were obtained using the same instrument and the following procedure: a sample was heated to the desired isothermal temperature in the range 673–794 K with a heating rate of 160 deg/min; under isothermal conditions the change of sample mass with the time was measured and only the initial period of isothermal pyrolysis was taken for the determination of the kinetic parameters.

Non-isothermal/isothermal analysis

Combined non-isothermal/isothermal analysis was usually performed using the following procedure: a total pyrolysis time of 57 min equal to the total time of NI-TG when a 10 deg/min heating rate was applied in the range of temperatures 303–873 K. A sample of oil shale was heated from 303 to 523 K at 20 deg/min, followed by holding the sample at 523 K for 5 min, then again from 523 to 623 K at 20 deg/min followed by holding the sample at 623 K for the next 2.5 min. The same procedure of non-isothermal heating at 20 deg/min was applied between 623 and 673 K (holding at 673 K for 2.5 min), 673 and 723 K (holding at 723 K for 2.5 min), 723 and 773 (2.5 min isothermally at 773 K), 773 and 803 (1.5 min of isothermal pyrolysis at 803 K) and finally heating the sample from 803 to 873 K at 20 deg/min. Such a procedure gives the above-mentioned total time of combined NI/I pyrolysis of 57 min. Typical TG curves for NI pyrolysis obtained at different heating rates are shown in Fig. 1a (curves 1–4), together with a step-descent curve (marked line 5, Fig. 1a) which corresponds to the pyrolysis performed using the explained NI/I procedure. The mass changes at different isothermal temperatures (523; 623; 673; 723; 773 and 803 K) are shown in Fig. 1a by the line normal to the axis of temperature, and in Fig. 1b by the continual lines (1–6) represented as Δm vs. time, as well as Δm vs. temperature for the isothermal and on-isothermal part of the pyrolysis, respectively.

Mathematical procedures

The procedures used in the determination of NI-TG derived kinetics correspond to the method of Doyle (1961) and Gorbachev (1975) when the first order reaction Eq. (1) is applied:

$$-\ln\left(-\ln\frac{1-X_K}{T^2}\right) = -\ln\left(A\frac{R}{q}(E+2RT)\right) + \frac{E}{RT} \quad (2)$$

where X_K = the conversion degree of kerogen calculated on the basis of the mass change of the sample at different temperatures or times;

$$X_K = (m_T - m_0)/f_1 m_0$$

T = temperature, K

A = frequency factor, s^{-1}

R = 8.314 J/mol·K

q = heating rate, K/s

E = activation energy, J/mol

The conversion values of the A, CR and K samples, calculated as described, were used for making a plot based on Eq. (2) and, hence, for determining the activation energy (from the slopes) and the frequency factor (from the intercept) in the range where the plot is linear.

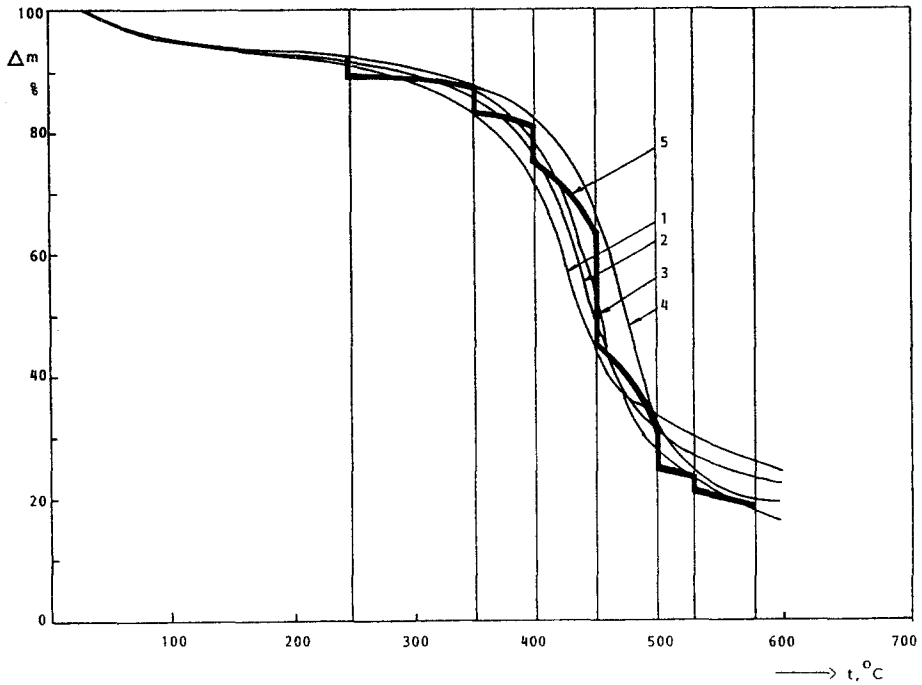


Fig. 1a TG curves for NI (heating rate; 1=2.5; 2=5; 3=10 and 4=20 deg/min) and combined NI/I analysis (curve 5) for sample A

The procedure used by Pan *et al.* (1985) was applied for the analysis of data derived by I-TG, based on the very well known integral method of analysis:

$$-\ln(1 - X_K) = k_T t \quad (3)$$

where: $k_T = A \cdot \exp(-E/RT)$, s^{-1} reaction rate constant, t = time, s.

Non-isothermal/isothermal analysis

The analysis of experimental data of NI/I pyrolysis is explained with all necessary details for the experiment performed using sample A under the following conditions: non-isothermal heating to the first isothermal temperature (30–523 K), as well as between all other isothermal temperatures (523–623;

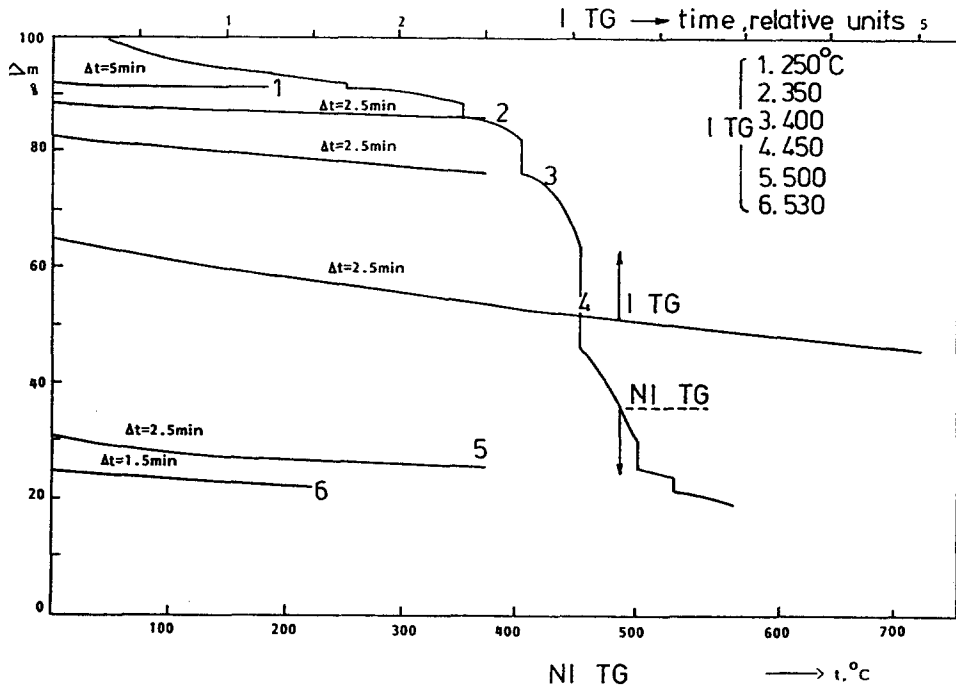


Fig. 1b TG curves of NI/I analysis (sample A)

623–723; 723–773; 773–803 and 803–853 K) at a heating rate of 160 deg/min; isothermal pyrolysis at 523, 623, 723, 773, 803 and 853 K in duration of 35 s at each temperature.

The experimental data obtained by NI/I TG were analysed using the integral method (Eq. (3)), i.e. by applying the same procedure as that described for I-TG. However, there are two possibilities for determining X_K , the conversion degree of kerogen. According to the first, X_K is calculated on the same principles used for NI and I-TG by determining the actual mass of kerogen (m_T) and knowing the initial mass of kerogen present in the oil shale sample, as well as the stoichiometric coefficient f_1 (Skala *et al.*, 1989).

The second one, which is also used for X_K determination at specific isothermal conditions, takes into account only one part of the organic materials (kerogen and bitumen) from the oil shale which could be converted to the products (P and R) at conditions very close to the isothermal temperature used for NI/I TG. Following such a procedure X_K' at 523 K was calculated taking into account the actual mass change at this temperature compared to the detected cumulative mass change in the temperature interval 523–623 K, at 623 K to the cumulative

mass change in the interval 623–723 K and so on. Thus, the total mass of organic materials is divided into a few subfractions, e.g.:

$$m_o = \sum \Delta m_{i, o(\Delta T_i)}$$

$$i = 523, 623, 723, 773, 803 \text{ and } 853 \text{ K and}$$

$$\Delta T_i = 523-623; 623-723; 723-773; 773-803; 803-853 \text{ and } 853-873 \text{ K} \quad (4)$$

Analysis of the experimental data based on the application of the X_K or X_K' values for sample A is shown in Figs 2a and 2b.

The advantage of the procedure for determining the X_K' value is that the information regarding the mass change during the initial period of pyrolysis at some isothermal temperature (T_i), when compared to the possible mass change in a narrow temperature interval ($\Delta m_{i(T_i)}$) gives the necessary information for determining the actual values of the stoichiometric coefficient f_1 in Eq. (1). Namely, f_1 is a simple measure of the yield of volatile compounds (gas and liquid) and, obviously, is not a constant during NI-TG (Charlesworth, 1985). The average value of f_1 , determined from an actual mass at the end of NI-TG is 0.74, 0.35 and 0.60 for samples A, CR and K, respectively. According to the results of

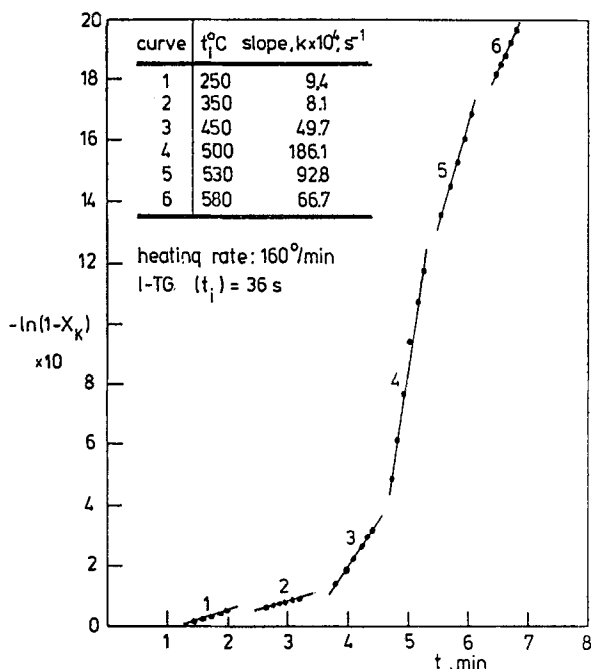


Fig. 2a Integral method applied using X_K

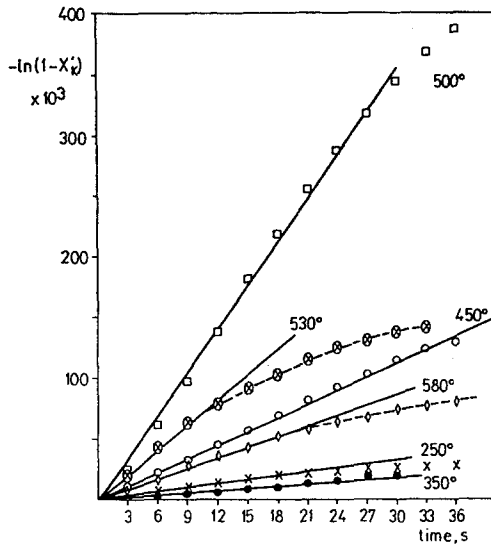
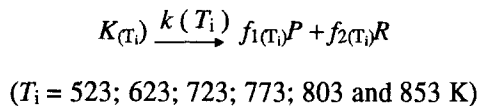


Fig. 2b Integral method applied using X_K'

NI/I TG and the proposed method for calculating f_1 , it is evident from the data presented in Fig. 3, that the yield of gas and oil varies with pyrolysis temperature.

The largest values of $f_1 (=1)$ in all the investigated samples are registered at the beginning of pyrolysis, while in the range of the fast decomposition of organic materials (usually above 723 K), i.e. in the vicinity of the temperature at which DTG-max occurs, f_1 is only slightly larger than the average value. At high temperatures f_1 drops below 0.5 or lower which can be explained by the fact that the main processes at temperatures above 500° are coking and cracking. Finally, the proposed method for X_K' and f_1 determination leads to the postulation of a complex reaction scheme of kerogen pyrolysis:



Results and discussion

The determined values of the activation energy in this study, as well as those recently published, are shown in Table 1.

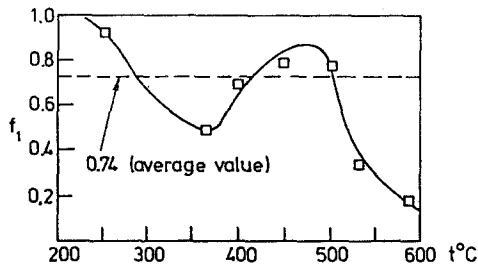


Fig. 3 The change of the stoichiometric coefficient f_1 with temperature (sample A)

Some discrepancies in the activation energies determined by different methods of TG were observed. Also, different results were obtained with the same sample (A) when applying NI-TG which was mainly caused by different periods in which this sample was analysed. Namely, it is well known that the slow reaction of oil shale oxidation causes sample ageing. Also, the NI-TG of sample A in the present work and of those recently published (Skala *et al.* 1987) were performed using different instruments and flow rates of carrier gas. Also, the slope of the linear part of Eq. (2) varied with heating rate during NI-TG (Table 1) which is a consequence of the very complex mechanism of oil shale pyrolysis.

However, when the results of I-TG were critically examined, a drawback of such an analysis was found regarding the procedure applied for determining the reaction rate constant in conventional thermobalances (Skala *et al.*, 1988). Namely, in the case of I-TG the specific procedure for getting the desired isothermal temperature (heating rate >160 deg/min) at which the mass change of the sample was analysed, could not suppress the decomposition of the part of the organic material before reaching isothermal conditions. There is also an increased mass change at the beginning of I-TG caused by the relatively intense degradation of organic compounds, especially of that which can also be observed at lower temperatures but requires more time. Thus, at the beginning of screening the pyrolysis process isothermally, such increased degradation obviously leads to higher values of reaction rate constant and, consequently, to higher activation energies as compared to those obtained by applying NI-TG.

Combined non-isothermal/isothermal pyrolysis avoids some of the drawbacks of I-TG, and also enables the determination of a complex reaction scheme which can be used for the mathematical simulation of the pyrolysis process in the whole range of temperatures at which oil shale is pyrolyzed.

Table 1 The activation energies calculated from NI, I and NI/I TG data

Sample	Heating rate / K/min					Remarks
	2.0	2.5	5.0	10.0	20.0	NI TG
A	—	79.8	78.9	85.8	84.5	This work
A	102.6	—	113.0	117.4	—	Skala <i>et al.</i> (1987)
				125.7		
CR	—	68.1	82.2	75.9	81.7	Skala <i>et al.</i> (1988)
K				55.2	93.6	Skala <i>et al.</i> (1990)
K			65.6	72.4	102.3	Skala <i>et al.</i> (1988)
						I TG
						(673–794 K)
A				141.3		Skala <i>et al.</i> (1988)
CR				91.1		Skala <i>et al.</i> (1988)
K				72.5		Skala <i>et al.</i> (1988)
						NI/I TG
A				55.3		this work, using X_K
				43.1		this work, using X_K'
CR				43.4		this work, using X_K
				37.2		this work, using X_K'
K				41.6		this work, using X_K
				35.0		this work, using X_K'

Conclusions

1) The obtained results show that the largest activation energies were detected by using I–TG, while combined NI/I TG gave the smallest values. In all the examined samples and performed TG analysis (NI, I, NI/I) there was an increase in the activation energy with increased content of paraffinic structures in the oil shale (kerogen type I).

2) Combined NI/I TG is a promising procedure for TG, since only a small number of experiments is required for determining the activation energy of the pyrolysis process, as well as for postulating such a mechanism of pyrolysis in which changeable yields of the volatile compounds (gas or oil) with temperature can be incorporated in the model for the mathematical simulation of the pyrolysis process.

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Zusammenfassung — Die im allgemeinen benutzte Kinetikgleichung in der Thermoanalyse von Ölschieferpyrolyse wurde auf der Grundlage einer einfachen kinetischen Gleichung erster Ordnung der Kerogenzersetzung erhalten. Mittels nichtisothermer (NI) oder isothermer (I) TG kann sowohl die Aktivierungsenergie als auch die Reaktionsgeschwindigkeitskonstante der Ölschieferpyrolyse bestimmt werden. Die unter Anwendung von NI oder I ermittelten kinetischen Parameter ermöglichen jedoch keine gute Voraussage des Kerogenumsatzes bei anderen Bedingungen.

Es werden hier die Vergleichsergebnisse aus NI- bzw. I-TG von verschiedenen Ölschiefern als auch die Auswirkungen auf die sogenannte kombinierte nichtisotherme und isotherme TG (NI/I) besprochen. Die erhaltenen Ergebnisse zeigen, daß ein Mechanismus angenommen werden muß, der auf einem komplexen Reaktionsschema aus mehr als aus einer einfachen Reaktion basiert.